CLUES ON ACID-SULFATE ALTERATION AND HEMATITE FORMATION ON EARTH AND MARS FROM IRON ISOTOPIC ANALYSES OF TERRESTRIAL ANALOGUES FROM HAWAII. N. X. Nie[1], N. Dauphas[1], and R. V. Morris[2], [1]Origins Lab, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, Chicago IL 60637 (xike@uchicago.edu), [2]NASA Johnson Space Center, Houston TX 77058.

Introduction: The Mars Exploration Rover mission revealed the presence of rocks and minerals indicative of water-rock interactions on Mars. A range of mineralogies have been identified, including hematite spherules (i.e., blueberries), jarosite, Mg-, Ca-sulfates, silica-rich materials and silicate relics from basaltic rocks. The mineral assemblages have been interpreted to be derived from acid-sulfate alteration of basaltic materials [1, 2]. Indeed, the chemical compositions of rocks and soils at Home Plate in Gusev Crater follow the trends expected for acid-sulfate alteration [3, 4].

While concretions from the Navajo sandstone in Utah provide a good field analogue to Martian blueberries, they formed in very different conditions [5, 6]. Hematite spherules and altered basaltic tephra from Hawaii volcanoes provide a very good terrestrial analogue to Martian sulfur-rich deposits, meaning that the chemical pathways responsible for the formation of those spherules may have been similar [7, 8]. They were formed by acid-sulfate alteration of basaltic materials from volcanoes. Their mineral assemblages including hematite, jarosite, alunite and other sulfates, and basaltic precursors are comparable to the source rocks on Mars. We performed a detailed Fe isotope study of Hawaii tephras and hematite spherules to understand the formation of hematite and sulfate deposits on Mars. This study will also provide an interpretive framework to iron isotope analyses of Martian blueberries if some samples are ever returned to Earth.

Samples and Methods: Samples are from two localities in Hawaii: Sulfur Bank (HWSB) and Mauna Kea volcano (HWMK). The Sulfur Bank sample HWSB820 [9] is a tholeiitic basalt sampled in the vicinity of an active fumarole that has led to acid-sulfate alteration of the rock. However, since the rock was partially buried in the ground, acid-sulfate alteration affected more its exposed top part but not much the bottom part, producing a color gradation from white to grey to black (top to bottom). The rock was sliced to 9 rock slabs with ~1 cm thickness. Each of the slabs has been measured for Fe isotopes.

The HWMK samples include both tephra samples and hematite spherules. Tephras consist of unaltered tephras, acid-sulfate altered tephras (including jarosite-bearing tephra and sulfate- and phyllosilicate-bearing tephra), and tephras that experienced other types of alteration (such as low-T palagonitic alteration or high-T dry oxidation). A hematite spherule concentrate was extracted from a sulfated tephra HWMK745R [8] by grinding a spherule-rich portion, dry sieving and centrifugation. Fifteen individual spherules ranging in diameter from 25 to 50 µm were hand-picked from the concentrate in water under a binocular microscope with a 10 µL pipette.

Iron isotopic analyses of the samples were conducted at the Origins Lab of the University of Chicago, following methods described in [10]. For HWSB820 slabs and HWMK tephras, approximately 10-20 mg of each sample was digested with $HF-HNO_3-HClO_4$ method. The spherule concentrate has a high Fe content (~36 wt %), therefore about 1 mg aliquot was digested. Iron was separated from matrix elements and purified with AG1-X8 resin twice, and then measured for isotopes using a Thermo Scientific Neptune MC-ICPMS. Individual spherules were digested and measured individually without any purification, as the chemistry blank would have represented a significant fraction of the analyzed iron.

Results: The nine slabs of HWSB820 show a range of $\delta^{56}Fe$ values ($^{56/54}Fe$ ratio relative to IRMM-014) from +0.22 to +0.94 ‰, correlated with their Fe/Ti ratios (Fig. 1). HWMK tephra samples also show variable Fe isotopic compositions, depending on the alteration type. Unaltered tephras have Fe isotopic compositions similar to other OIBs, with $\delta^{56}Fe$=+0.15 ‰ on average. Acid-sulfate altered tephras have variable $\delta^{56}Fe$, from +0.11 to +0.49 ‰. Samples that experienced other alteration processes than acid-sulfate alteration have values similar to unaltered tephras, with an average of +0.12 ‰.

The hematite spherule concentrate has a heavy $\delta^{56}Fe$ value of +0.42 ‰. All individual spherules appear to have identical Fe isotopic compositions to the spherule concentrate. Since each spherule contain only very small amount of Fe (tens to hundreds nanogram), their $\delta^{56}Fe$ values have bigger uncertainties, which decrease as the Fe quantity increases.

Discussion: Tephras that are associated with acid-sulfate alteration show variable and in general heavier Fe isotopic compositions compared to unaltered tephras and tephras altered by other processes. Therefore, acid-sulfate alteration process should drive the liquid to have a lighter Fe isotope signature than the alteration residue. The 9 slabs from the single rock HWSB820 show a very good Rayleigh-type fractionation (Fig. 1). The slab least affected by acid-sulfate

alteration (highest Fe/Ti ratio) has δ^{56}Fe value (+0.22 ‰) similar to the unaltered tephras (+0.15 ‰), while the most affected slab has the lowest Fe/Ti ratio and the highest δ^{56}Fe value of +0.94 ‰. Rayleigh fractionation simulation suggests that the Fe isotope fractionation between liquid and solid is -0.24 ‰.
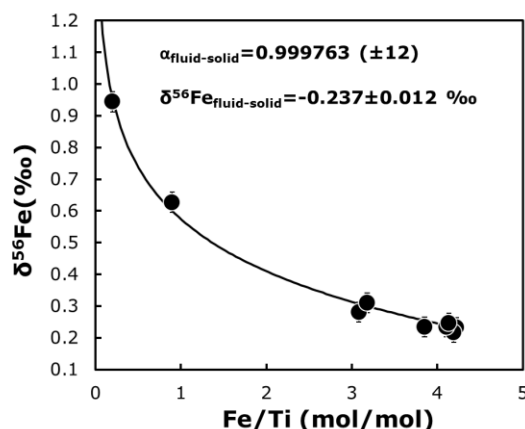
The individual spherules show identical δ^{56}Fe values, regardless of their sizes, suggesting that they are co-genetic, probably derived from the same Fe source. It has been suggested that the spherules could form either by 1) direct precipitation from the liquid produced by dissolution of basaltic material, or by 2) a two-step process involving precipitation of jarosite and other sulfates in a first step and hydrolysis of jarosite to form hematite in a second step [8]. Direct precipitation of hematite from a liquid would most likely produce rather heterogeneous Fe isotopic compositions. This is because the precipitated solid would presumably be unable to exchange isotopically with the liquid to maintain isotope equilibrium at all stages. Therefore a Rayleigh-type Fe isotope fractionation during precipitation is expected. Hematite spherules measured here seem to have identical δ^{56}Fe values (due to small Fe amount, uncertainties are big, but no correlation between Fe quantity and δ^{56}Fe values was found). Most likely, the δ^{56}Fe homogeneity of the spherules reflects isotope re-equilibrium during the formation of hematite through jarosite hydrolysis.

To produce the +0.4 ‰ isotopic composition of the hematite spherules through jarosite hydrolysis, jarosite should either have a similar isotopic composition, if its conversion to hematite is quantitative, or have a δ^{56}Fe value close to ~+0.9 ‰, assuming equilibrium fractionation between the two minerals and a fractionation factor of -0.5 ‰ [11, 12]. The isotope fractionation between jarosite and the fluid it precipitated from should thus be ~+0.5 ‰ or ~+1 ‰. Iron isotope fractionation during precipitation of jarosite from Fe(II)aq solution has not been investigated. However, experiments studying precipitation of Fe(III) oxide-hydroxide from Fe(II)aq solutions have shown that precipitates are always enriched in heavier Fe isotopes, by ~+1 ‰, regardless of oxidation paths (biotic, O_2-mediated or photo-oxidation) [13-15]. Jarosite precipitation could record similar isotope fractionation. If this is the case, the two-step process can readily produce the isotope signature measured in the hematite spherules.

The two-step process is applicable to the formation of hematite spherules and sulfate deposits on Mars. Thermodynamic modelling shows that jarosite and other sulfates on Mars could be produced by evaporation of acidic fluids produced by acid-sulfate alteration of basalts. After this, a pH-raising fluid recharge event could convert jarosite to hematite [2]. Therefore, hematite spherules and sulfates from Hawaii and from Mars appear to have formed in similar ways. This study provides some interpretative framework for iron isotope studies of future Mars sample return missions.

Conclusion: Iron isotope analyses of acid-sulfate alteration products from Hawaii show that acid-sulfate alteration process tends to enrich the fluid phase in light Fe isotopes compared to the solid phase, by -0.24 ‰ in terms of δ^{56}Fe values. The hematite spherules from Hawaii have δ^{56}Fe values consistent with a two-step formation process, that is, jarosite precipitation from fluids produced by acid-sulfate alteration of basalts followed by hydrolysis of jarosite to form hematite. This two-step formation scenario is similar to the formation of Martian hematite spherules, making further study of Hawaii analogue a very promising approach to understand Martian surface processes.

Fig. 1: *Iron isotope fractionation in the slabs of HWSB820 is consistent with Rayleigh fractionation, with a factor of -0.24 ‰ between fluid and solid in acid-sulfate alteration.*

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